

SEDIMENT PRECURSORS IN MIDDLE DISTILLATE FUEL INSTABILITY REACTIONS

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ABSTRACT

The specific molecules that initiate the reactions that lead to fuel sediments are difficult to isolate chemically. Several diverse mechanisms could be invoked to explain experimental findings: electron transfer initiated oxidation mechanisms, free radical hydroperoxide initiated oxidation mechanisms and soluble macro-molecular oxidation mechanisms. In actual practice, these specific reactions, in addition to many other mechanisms are simultaneously occurring. Results from our experiments demonstrate that acid catalyzed condensation reactions followed by a rapid increase in polarity caused by hydroperoxide induced oxidation steps can mimic the sedimentation processes observed in many middle distillate fuels.

INTRODUCTION

Instability can be thought of as an interactive process involving the four main functional groups listed in Figure 1. The difficulty arises in isolating the chemical importance of each functional group and specific mechanisms to the overall process. It is amazing that less than 1 ppm of the fuel itself is involved in the process that has the potential to be detrimental to a whole storage tank.

Figure 1. Functional Groups Involved in Incompatibility Reactions.

R-C=C-	+ R-N-	+ R-S-	+ R-O-O-
Hydrocarbon	Organo-Nitrogen	Organo-Sulfur	Organo-Oxygen
Alkenes	Indoles	Sulfonic Acid	Hydroperoxides
Indenes	Carbazoles	Thiols	Dissolved Oxygen
Monocyclics	Pyrroles	Disulfides	Carboxylic Acids
Bicyclics	Quinolines	Sulfoxides	Peroxides
Polycyclics	Pyridines	Sulfides	Aldehydes
	Piperdines	Thiophenes	Alcohols

RESULTS AND DISCUSSION

Based on sediment analysis, it is a reasonable contention that the incompatibility of fuels can be explained by the functional groups listed in Figure 1. A myriad of chemical reaction pathways could be derived from these various functional groups in the following mechanisms; the hydroperoxide initiated polymerization oxidation reactions with olefins to produce gums; an electron-transfer-initiated-oxygenation (ETIO)², followed by reactions that result in degradation; the hydroperoxide oxidation of organo-sulfur compounds to sulfonic acids which then subsequently catalyze condensation reactions between the other functional groups present leading both to incorporation of heteroatoms and a simultaneous increase in polarity and molecular weight and thus precipitation from the fuel; and finally, the same reaction sequence could be used to describe the soluble macromolecular oxidatively reactive species (SMORS)¹. The exact chemical composition of the sediment will depend on the chemical composition of the particular fuel. Individual fuels display unique sediments. These functional groups are involved in both chemical and physical processes that leads to deleterious solids. However, certain compound classes are observed to be common to all sediments. Thus, the presence of these heteroatomic compound classes can be used as incompatibility predictors. All of these processes depend on dissolved oxygen and/or hydroperoxides to initiate the processes leading to degradation. Remove molecular oxygen and/or hydroperoxides, usually by clay filtration,

and fuel compatibility will improve dramatically⁵.

In the sedimentation process, a major unknown is the identity of the soluble precursor to these sediments. Figure 2 illustrates both the chemical and physical processes that lead to sediment formation. These precursors are in the early stages of research. These precursors, SMORS, could be the result of the catalytic cracking process of the petroleum crude. A classical chemistry description of SMORS is that they are derived from monomers in the fuel itself. However, this description fails because of the inability to link any SMORS precursors in the fuel to the insolubles formed in the fuel. If this intermediate could be chemically elucidated, the sedimentation process observed in practically all middle distillate fuels, incompatibility would be better understood¹.

Figure 2. Chemical and Physical Processes that Lead to Insoluble Products

<u>CHEMICAL PROCESSES</u>	<u>PHYSICAL PROCESSES</u>
Fuel	Coalescence
Middle	insoluble products
Distillate	1000 - 5000 °A
Fuel	
↓	↓
Soluble Macromolecular Intermediate	Surface Effects
fuel oxidation intermediates	Collect on walls
fuel soluble	and
increasing polarity	fuel lines
N, O, and S incorporation	
↓	↓
Insoluble Products	Temperature Effects
fuel sediments	extensive oxidation
high heteroatom content	at high temperatures
Molecular weight >>500	leads to coking

It is thus easy to imagine the situation in which a blended fuel could pass the required accelerated test method, ASTM D2274, at the refinery, but then form large amounts of insolubles when it reaches the consumer⁶. Because of the increasing use of blended stocks, there is no "one" middle distillate fuel consequently, there is also no "one" mechanism of degradation. However, the mechanism and the functional groups involved will give a general but not specific mode of incompatibility. The key reaction in all incompatibility processes is the generation of the hydroperoxide species from dissolved oxygen. Once the molecular oxygen and/or hydroperoxide concentration starts to increase, macromolecular incompatibility precursors can form in the fuel. Acid/base catalyzed condensation reactions then rapidly increase the polarity, chemical incorporation of heteroatoms, and the molecular weight.

Three related, but separate reaction regimes can be used to explain the chemical incompatibility that is occurring during the different stages that a fuel goes through in its lifetime. At the refinery or in the early life of a fuel, SMORS, incompatibility can best be explained by acid/base catalyzed condensation reactions of the various organo-nitrogen compounds in the individual blending stock themselves. These acid/base catalyzed processes are usually very rapid reactions with practically no observed induction time period. When the fuel is transferred to a storage tank or other holding tank incompatibility can be explained by a second slow mechanism; the free-radical hydroperoxide induced polymerization of active olefins (gums). This is a relatively slow reaction, because the increase in hydroperoxide concentration is dependent on the dissolved oxygen content. These gums can be quite deleterious to combustion machinery. The third incompatibility mechanism involves; the degradation reactions observed when the fuel is stored for one or more years. Extended storage is a common practice for the military. The incompatibility process can be explained by a complicated set of reactions. It involves first the buildup of hydroperoxide moieties after the gum reactions; then a free-radical reaction with the various organo-sulfur compounds present that can be oxidized to sulfonic acids; then reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reactions. This is the slowest of the reactions because of the hydroperoxide induction period and the subsequent oxidation of the

organo-sulfur compounds.

A matrix involving time, temperature, heteroatoms, hydroperoxides, and other reactive species present in fuels in the context of accelerated storage is complicated. Accelerated fuel stability tests are important to both producers and users of fuels so an understanding of these interactions is important. Model dopant studies provide a method for isolating some of these variables. Model studies to define chemical incompatibility work well with gasoline and jet fuels. With chemically more complicated diesel fuels, they are somewhat less reliable. With relatively simple fuel, model studies set the parameters for incompatibility. Thus tests performed to mimic long-term storage give results that are definitive as long as the temperature employed is low enough not to initiate homolytic hydroperoxide reactions (<100°C). Higher temperatures enable storage tests to be completed in the minimum time, a producer advantage. The significance of the accompanying uncertainty of the observed sediment-producing processes in relation to the real ambient storage conditions may be dominant, a user disadvantage. Much of the early work has concentrated on the use of organo-nitrogen and sulfur compounds, both basic and non-basic, as dopants. It was demonstrated that the solid formed from these dopants were similar to the solids obtained from shale liquids themselves. The promotion of sediment formation by these dopants has been reported to be a facile process.

In a series of papers starting in 1987, results were reported that explained some of the inconsistencies observed with deposit formation and sulfur compound interactions⁸. The authors show that the stability of an unstable middle distillate fuel was improved by treatment with sodium hydroxide. The subsequent addition of a sulfonic acid, 10 ppm of naphthalene sulfonic acid, restored the instability of the base washed fuel. A linear relationship between deposit formation and sulfonic acid concentration confirms that the formation of a strong acid is a limiting factor in storage instability. Further, the deposits generated by the sulfonic acid treatment were found to be identical from those formed from the fuel itself on storage. It was further reported that the chemical structures observed in the sediment precursors consisted of indoles linked to a phenalene ring system. In the particular diesel fuel studied, phenalene was detected. Oxidation products, i.e., various phenalenones, were observed to increase in concentration as the fuels were aged under ambient storage conditions. This appears to be a major step forward in the chemistry of sediment formation. However, much more study is needed to extend this observation to other middle distillates.

ETIO results are primarily from model systems. No results or sediments based on fuel system ETIO are available. For ETIO to be a viable concept in fuel degradation, two significant phenomena must be operative: a rate law based on oxygen order; lack of chemical response to both amine and phenolic free-radical inhibitors. Other model systems employing 3-methyl indole and the anthraquinone molecular ion have results that show ETIO operating in model systems.

The data in Table 1 show the results for a model system employing 3-methylindole and various acids present as co-dopants. A comparison of the sediment from the undoped to the carboxylic acid doped systems show a remarkable similarity in formula. Infra red and mass spectral results show that the carboxylic acid groups are not incorporated in the sediment⁹. In the case of the strong acid dodecylbenzene sulfonic acid (DBSA) however, the results are quite different. The sediment generated by this acid incorporated the DBSA moiety into the sediment, this was confirmed by ¹³C nmr and field ionization mass spectrometry.

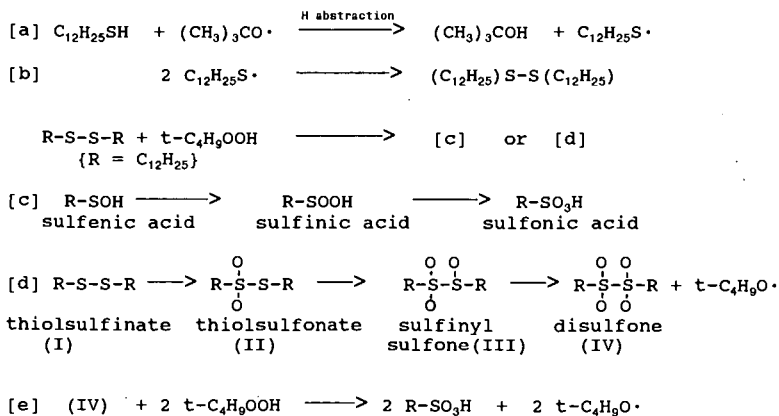
Table 1. Elemental Analysis Data for Sediments Derived from 3-Methylindole in a Middle Distillate Fuel with Added Co-Dopants

Co-Dopant*	Percent by Weight					S	Empirical Formula
	N	C	H	O			
None	5.36	72.63	5.88	16.13	-		C _{15.8} H _{15.2} NO _{2.8}
Acetic acid	5.57	72.72	5.92	15.77	-		C _{15.2} H _{14.8} NO _{2.5}
Hexanoic acid	5.65	72.16	5.78	16.41	-		C _{14.6} H _{14.2} NO _{2.4}
Decanoic acid	5.81	72.55	5.76	15.88	-		C _{14.6} H _{13.8} NO _{2.4}
Dodecylbenzene sulfonic acid	5.10	73.33	8.20	5.65	8.45		C _{18.4} H _{30.3} N _{1.3} SO _{1.3}

* Concentration dopants = 3.21×10^{-2} M
3-MI = 450 ppm N

The organo-sulfur moieties that have proved to be the most damaging are the thiols, disulfides and sulfonic acids. These results and those from other studies have indicated that some sulfur compounds might be inhibitors for controlling hydroperoxide formation in middle distillate fuels. However, they control the peroxides by undergoing oxidation to sulfonic acids as depicted in Reaction Scheme 1. Partially oxidized sulfur species, such as sulfoxides and sulfones are not generally deleterious¹¹. Thiophene related compounds are very resistant to oxidation and are thus harmless in the stability process. Sulfonic acids are the most deleterious dopant that we have studied^{11,12}. Thiols are excellent radical scavengers in both fuels and in model fuel systems¹². The most probable mechanism for the reaction sequence for a thiol involved a hydrogen abstraction step by a t-butoxy radical that was generated from a peroxide species, such as t-butyl hydroperoxide, t-C₄H₉OOH. Once a disulfide is generated, steps [a and b], one or both pathways, [c and e], exists for sulfonic acid formation.

Reaction Scheme 1. Reaction Pathways of Hydroperoxides and Disulfides to Produce Sulfonic Acid



However, sulfenic acids and sulfinic acids have not been observed either in model systems or in fuels. The partially oxidized species, products I - IV in step [d], have been observed in fuels and model oxidation systems¹¹. Product IV, a disulfone, by reaction with a mild oxidant, hydroperoxides, generates the corresponding sulfonic acid, step [e].

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